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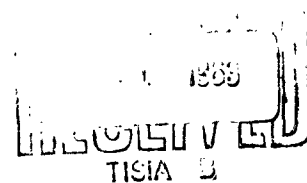
ONR TECHNICAL REPORT NO.53

Project: NR 356-378

Contract: Nonr 3357(01)

A GAUSSIAN THEORY OF ORIENTATION CORRELATIONS
IN CRYSTALLINE POLYMERIC SOLIDS

December 26, 1962



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FOREWORD

This report is the manuscript of a paper that will be presented before the Division of High Polymer Physics of the American Physical Society in St. Louis, March, 1963 and will subsequently be submitted for publication in the *Journal of Applied Physics*.

The first part of this is identical with a part of our previous Technical Report No. 25 on "The Relative Orientation of Crystalline and Amorphous Regions in Polyethylene". In this paper, the approach initiated in this manuscript is extended to three dimensions.

A GAUSSIAN THEORY OF ORIENTATION CORRELATIONS IN CRYSTALLINE POLYMERIC SOLIDS*

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INTRODUCTION

In an undrawn film of a crystalline polymer such as polyethylene, the crystals are arranged with an average random orientation. This is a macroscopic average. Within small regions there is a preferential orientation in a particular direction, but these small regions are randomly oriented with respect to each other. Thus, the crystals would be arranged in a kind of domain structure similar to that which exists in metals. The distinction between random and domain structures is shown in Figure 1. Light scattering studies from this laboratory^{1,2,3} indicate that the principal cause of scattering from films of crystalline polyethylene is the refractive index heterogeneity produced by orientation fluctuations among such domains. This interpretation is consistent with electron microscope observations^{4,5} and with interpretations of low angle x-ray diffraction patterns.⁶

From Fourier inversions of polarized light scattering data, one may obtain an orientation correlation function $f(r)$ which is defined in Eq. (1)^{2,3,7}

$$f(r) = \left\langle \frac{3 \cos^2 \theta_{ij} - 1}{2} \right\rangle_r \quad (1)$$

The polymer is considered to be subdivided into volume elements, each of which is small compared with the wavelength of light. These may contain both crystalline and amorphous material. Because of the preferred orientation of the polymer within these volume elements, they will be anisotropic. We will assume that they have a cylindrical symmetry with a single unique direction or principal optic axis. θ_{ij} is the angle between the optic axis of the i th volume element and that of the j th. The brackets in Eq.(1) designate an average over all pairs of volume elements separated by a constant scalar distance, r . If $r = 0$, it is apparent that the two volume elements become identical and must have parallel optic axes, so that $\theta_{ij} = 0^\circ$ and $f(r) = 1$. Whereas, if $r = \infty$, θ_{ij} will assume random values, $\cos^2 \theta_{ij} = 1/3$, so that $f(r) = 0$. Thus, $f(r)$ decreases from 1 to 0 as r increases from 0 to ∞ , as indicated in Fig. 2. The rate at which $f(r)$ decreases with increasing r determines the size of the domain of correlated orientation. For many systems, the correlation functions may be fitted by the empirical equation^{8,9}

$$f(r) = \exp (-r/a) \quad (2)$$

* Supported in part by contracts with the Office of Naval Research and the Atomic Energy Commission and in part by grants from the Plax Corporation and the Petroleum Research Fund.

where the parameter, a , is a measure of the domain size and is a persistence distance of orientation correlation. The greater a , the larger the domain. It is found that a depends on the temperature of crystallization and is of the order of 3000 Å units for a typical polyethylene sample. This is about ten times larger than a single crystal and means that for an average distance of about five crystal diameters away from a given crystal in any direction, there is a tendency for correlation in orientation. This is somewhat analogous to the situation existing in a liquid, where the radial distribution function of density indicates crystal-like order for atoms close to a given atom, with a decrease in this order for greater distances.

The mechanism for establishment of these domains is apparent in terms of current theories of polymer crystal growth.^{10,11} On cooling a melt, the growth is initiated by the formation of an homogeneous or heterogeneous primary nucleus which rapidly grows to a size determined by the temperature of crystallization and by the perfection of the polymer chain. The continuation of the crystallization is dependent on the formation of more nuclei. It is easier, however, for these secondary nuclei to form in the vicinity of the primary nucleus than elsewhere in the polymer. Two reasons proposed for this are: a) dendrites emanating from the primary crystal or dislocations or surface imperfections serve as secondary nuclei^{12,13} and, b) strains imposed upon the surrounding amorphous material render it more capable of crystallizing. This nucleation growth mechanism results in crystals growing in clusters about primary nuclei rather than randomly throughout the polymer, and is consistent with the observed spherulite formation. Furthermore, it seems likely that these secondary nuclei will be preferentially oriented with respect to the primary nuclei, so that there will be some "slop" in the transmission of orientation from one crystal to the next, so that with increasing distance away from any crystal there will be a decrease in the correlation of orientation. In fact, when this is extended to dimensions comparable with the size of a spherulite (perhaps 100 to 1000 times the crystal size), this gives rise to circular symmetry of crystal orientation rather than preferred orientation in any particular direction. Over distances of perhaps five crystal sizes within the spherulite, however, there will be preferential orientation in a given direction, the orientation becoming poorer with greater distance.

ONE DIMENSIONAL THEORY FOR $f(r)$

Consider a one-dimensional array of crystals (Fig. 3). Let crystal 0 be the primary nucleus in this array which is oriented in the vertical direction at an angle of $\theta = 0^\circ$. The crystal adjacent to this, crystal 1, tends to be parallel to crystal 0 but they differ in orientation by an amount δ . For simplicity, we will assume that it will lie at an angle of $+\delta$ or $-\delta$ with respect to crystal 2. Thus, there will be random fluctuations in the orientations of each crystal with respect to its nearest neighbor, but these cannot exceed δ . It is apparent that the correlation of orientation becomes poorer between the n th and 0 th one as n increases, so that this model exhibits short range correlation of orientation, but long range randomness. The probability that the n th crystal will make an angle of θ with respect to the 0 th one may be solved by the classical "problem of the random walk".

Assume that the crystals are equally spaced a distance, d , apart. If the n th crystal is at a distance r away from the 0 th crystal, the number of intervals between the n th crystal and the 0 th crystal is given by

$$n = \frac{r}{d} \quad (3)$$

Since for each of these intervals the angle θ will change by either $+\delta$ or $-\delta$ the total change in θ during the interval, r , will depend upon the difference between the number of $+\delta$ and $-\delta$ changes. Let us call this difference n .

$$x = (n_+) - (n_-) \quad (4)$$

so that the angle of the n th crystal is given by

$$\theta_n = x\delta \quad (5)$$

The probability of a given number of n_+ and n_- for a total number of steps, n , is obtained by the usual "random walk" statistics¹⁴ and is given by

$$P(x) = \frac{Cn!}{(n_+)! (n_-)!} = \frac{Cn!}{\left[\frac{n+x}{2}\right]! \left[\frac{n-x}{2}\right]!} \quad (6)$$

where C is a constant of proportionality. By using Stirling's approximation, one obtains the usual result

$$P(x) = \exp(-x^2 / 2n) \quad (7)$$

The average value for $\cos^2 \theta$ for two volume elements separated by distance r corresponding to the n steps is given by*

$$\langle \cos^2 \theta_n \rangle = \frac{\int_{-\infty}^{\infty} \cos^2 \theta_n P(x) dx}{\int_{-\infty}^{\infty} P(x) dx} \quad (8)$$

On using Eq. (5) for θ_n and Eq. (7) for $P(x)$, one gets

$$\begin{aligned} \langle \cos^2 \theta_n \rangle &= \frac{\int_{-\infty}^{\infty} \cos^2 (x\delta) e^{-x^2/2n} dx}{\int_{-\infty}^{\infty} e^{-x^2/2n} dx} \\ &= \frac{1}{2} \left[1 + e^{-2n\delta^2} \right] \end{aligned} \quad (9)$$

If one uses Eq. (3) for n and substitutes the parameter a defined by

$$a = \frac{d}{2\delta^2} \quad (10)$$

then one obtains

$$\langle \cos^2 \theta_n \rangle = \frac{1}{2} \left[1 + e^{-r/a} \right] \quad (11)$$

*The integration should actually be between the limits of $x = \pm \pi/\delta$. However, it is assumed that $\exp[-x^2/2n]$ decreases sufficiently rapidly with increasing x that negligible error will be made in integrating to $\pm \infty$.

From this, it is apparent that the average of $\cos^2 \theta$ varies from 1 at $r = 0$ (indicating parallel orientation of the crystals) to $1/2$ at $r = \infty$ (indicating random orientation). An average of $\cos^2 \theta = 1/2$ where θ varies in a plane corresponds to random orientation; that is, no correlation in orientation of the crystals. For planar variations of angles, the orientation function defined in Eq. (1) should be replaced by

$$f(r) = \langle 2 \cos^2 \theta_{ij} - 1 \rangle_r \quad (12)$$

so that $f(r)$ varies from 1 to 0 as $\cos^2 \theta$ average varies from 1 to $1/2$. On using the value of $\cos^2 \theta$ from Eq.(11) in this, one obtains for $f(r)$

$$f(r) = e^{-r/a} \quad (13)$$

which is identical with Eq. (2). The correlation distance, a , now defined by Eq. (10) is a quantity which is proportional to the intercrystalline distance which varies with crystal size and which varies inversely with δ . (The uncertainty in orientation of adjacent crystals.)

EXTENSION TO THREE DIMENSIONS

For three-dimensional correlation, a cubical lattice model will be used where each cell has dimension d (Fig. 4). The scattering elements will again be assumed to be uniaxial and characterized by the orientation of their optic axes. Consider two volume elements O and n lying along the same lattice row and separated by a distance $r = n d$. We will assume that crystals in adjacent lattice cells may differ in orientation by a small angle δ , as before, but that an azimuthal angle ϕ (Fig. 5) may assume all values with equal probability. Let $\mathbf{a}_0, \mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n$ be unit vectors in the $0^{\text{th}}, 1^{\text{st}}, 2^{\text{nd}}$ and n^{th} cells pointing in the optic axis direction. The angle θ_{on} between the vectors \mathbf{a}_0 and \mathbf{a}_n may then be obtained from

$$\cos \theta_{on} = (\mathbf{a}_0 \cdot \mathbf{a}_n) \quad (14)$$

and the orientation function may be obtained from

$$f(r_n) = \frac{3 (\mathbf{a}_0 \cdot \mathbf{a}_n)^2 - 1}{2} \quad (15)$$

The averaging is over all internal rotation angles ϕ_i weighted equally.

The vector \mathbf{a}_1 may be obtained from \mathbf{a}_0 by

$$\mathbf{a}_1 = |T_1| \mathbf{a}_0 \quad (16)$$

where T_1 is the transformation matrix given by ¹⁵

$$\begin{vmatrix} T_1 \end{vmatrix} = \begin{vmatrix} \cos \delta & -\sin \delta \cos \phi_1 & \sin \delta \sin \phi_1 \\ \sin \delta & \cos \delta \cos \phi_1 & -\cos \delta \sin \phi_1 \\ 0 & \sin \phi_1 & \cos \phi_1 \end{vmatrix} \quad (17)$$

Similarly, $a_2 = |T_2| a_1 = |T_2| |T_1| a_0 \quad (18)$

and $a_n = |T_n| |T_{n-1}| \cdots |T_2| |T_1| a_0 \quad (19)$

where

$$\begin{vmatrix} T_i \end{vmatrix} = \begin{vmatrix} \cos \delta & -\sin \delta \cos \phi_i & \sin \delta \sin \phi_i \\ \sin \delta & \cos \delta \cos \phi_i & -\cos \delta \sin \phi_i \\ 0 & \sin \phi_i & \cos \phi_i \end{vmatrix} \quad (20)$$

Since a_0 is a unit vector in the x direction or 1

$$(\overline{a_0 \cdot a_n})^2 = [1 \cdot |T_n| |T_{n-1}| \cdots |T_2| |T_1| 1]^2 \quad (21)$$

In terms of summation notation, this is given by

$$(\overline{a_0 \cdot a_n})^2 = \left[\sum_{i,j,k,\dots,s,t} \sum_i [a_{1i}]_n [a_{ij}]_{n-1} [a_{jk}]_{n-2} \cdots [a_{st}]_2 [a_{t1}]_1 \right]^2 \quad (22)$$

where $[a_{ij}]_{n-1}$ is the ij^{th} element of the $(n-1)^{\text{th}}$ transformation matrix $|T_{n-1}|$

If the azimuthal angles ϕ_i vary randomly and independently of each other, averages of the cross-products of the square of the above sum vanish giving (Appendix I)

$$(\overline{a_0 \cdot a_n})^2 = \sum_{i,j,\dots,s,t} \sum_i \left\{ \overline{[a_{1i}]_n^2} \overline{[a_{ij}]_{n-1}^2} \cdots \overline{[a_{st}]_2^2} \overline{[a_{t1}]_1^2} \right\} \quad (23)$$

where

$$\begin{aligned} \overline{[a_{ij}]_{n-1}^2} &= \begin{vmatrix} \cos^2 \delta & \sin^2 \delta \overline{\cos^2 \phi_{n-1}} & \sin^2 \delta \overline{\sin^2 \phi_{n-1}} \\ \sin^2 \delta & \cos^2 \delta \overline{\cos^2 \phi_{n-1}} & \cos^2 \delta \overline{\sin^2 \phi_{n-1}} \\ 0 & \sin^2 \phi_{n-1} & \cos^2 \phi_{n-1} \end{vmatrix} \\ &= \begin{vmatrix} \cos^2 \delta & 1/2 \sin^2 \delta & 1/2 \sin^2 \delta \\ \sin^2 \delta & 1/2 \cos^2 \delta & 1/2 \cos^2 \delta \\ 0 & 1/2 & 1/2 \end{vmatrix} = |B| \quad (24) \end{aligned}$$

This matrix is independent of n so that

$$\left| \overline{a_{ij}^2} \right|_{n-1} = \left| \overline{a_{jk}^2} \right|_m = \dots = \left| \overline{a_{st}^2} \right|_p = |B| \quad (25)$$

Thus,

$$\overline{(a_0 \cdot a_n)^2} = |100| |B|^{n-1} \begin{vmatrix} 1 \\ 0 \\ 0 \end{vmatrix} \quad (26)$$

where, for example,

$$B_{ik}^2 = \sum_j \overline{a_{ij}^2} \overline{a_{jk}^2} \quad (27)$$

where B_{ik}^2 is the ik^{th} element of the matrix $|B|^2$

The evaluation of Eq. (26) requires the development of a general expression for $|B|^m$. For this purpose, it is convenient to make the substitutions

$$\begin{aligned} x &= \sin^2 \delta \\ (1-x) &= \cos^2 \delta \end{aligned} \quad (28)$$

where x is small. Then Eq. (24) becomes

$$\begin{aligned} |B| &= \begin{bmatrix} (1-x) & 1/2 x & 1/2 x \\ x & 1/2(1-x) & 1/2(1-x) \\ 0 & 1/2 & 1/2 \end{bmatrix} \\ &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} + \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} x \\ &= |A_0| + |A_1| x \end{aligned} \quad (29)$$

where

$$|A_0| = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} \quad (30)$$

and

$$|A_1| = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} \quad (31)$$

$$\begin{aligned}
 |B|^2 &= (|A_0| + |A_1| x) (|A_0| + |A_1| x) \\
 &= |A_0||A_0| + |A_1||A_0| x + |A_0||A_1| x + |A_1||A_1| x^2 \\
 &= |A_0|^2 + |A_1| |A_0| + |A_0| |A_1| x + |A_1|^2 x^2
 \end{aligned} \tag{32}$$

Similarly,

$$\begin{aligned}
 |B|^3 &= |A_0|^3 + (|A_0|^2 |A_1| + |A_1| |A_0|^2 + |A_0| |A_1| |A_0|) x \\
 &\quad + (|A_1| |A_0| |A_1| + |A_0| |A_1|^2 + |A_1|^2 |A_0|) x^2 + |A_1|^3 x^3
 \end{aligned} \tag{33}$$

The value of $|A_0|^m$ may be obtained inductively since

$$|A_0|^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/4 & 1/4 \\ 0 & 1/4 & 1/4 \end{bmatrix} \tag{34}$$

and

$$|A_0|^m = \begin{bmatrix} 1 & 0 & 0 \\ 0 & (1/2)^m & (1/2)^m \\ 0 & (1/2)^m & (1/2)^m \end{bmatrix} \tag{35}$$

Similarly

$$|A_1|^2 = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 3/2 & -3/4 & -3/4 \\ -3/2 & 3/4 & 3/4 \\ 0 & 0 & 0 \end{bmatrix} \tag{36}$$

$$|A_1|^3 = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 3/2 & -3/4 & -3/4 \\ -3/2 & 3/4 & 3/4 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} -9/4 & 9/8 & 9/8 \\ 9/4 & -9/8 & -9/8 \\ 0 & 0 & 0 \end{bmatrix} \tag{37}$$

and generally

$$|A_1|^m = \begin{bmatrix} -(-3/2)^{m-1} & 1/2(-3/2)^{m-1} & 1/2(-3/2)^{m-1} \\ (-3/2)^{m-1} & -1/2(-3/2)^{m-1} & -1/2(-3/2)^{m-1} \\ 0 & 0 & 0 \end{bmatrix} \tag{38}$$

The product

$$|A_1| |A_0| = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} = |A_1| \quad (39)$$

Continuing

$$|A_1| |A_0|^2 = (|A_1| |A_0|) |A_0| = |A_1| |A_0| = |A_1| \quad (40)$$

Generally

$$|A_1| |A_0|^m = |A_1| \quad (41)$$

and

$$|A_0|^n |A_1| |A_0|^m = |A_0|^n |A_1| \quad (42)$$

Applying these results to (32) and (33) one obtains

$$|B|^2 = |A_0|^2 + (1 + |A_0|) |A_1| x + |A_1|^2 x^2 \quad (43)$$

and

$$|B|^3 = |A_0|^3 + (1 + |A_0| + |A_0|^2) |A_1| x + (2 + |A_0|) |A_1|^2 x^2 + |A_1|^3 x^3 \quad (44)$$

Extending this procedure gives

$$\begin{aligned} |B|^4 = & |A_0|^4 + (1 + |A_0| + |A_0|^2 + |A_0|^3) |A_1| x + (3 + 2 |A_0| \\ & + |A_0|^2) |A_1|^2 x^2 + (3 + |A_0|) |A_1|^3 x^3 + |A_1|^4 x^4 \end{aligned} \quad (45)$$

leading to the general case

$$\begin{aligned} |B|^m = & |A_0|^m + \left[|A_0|^{m-1} + |A_0|^{m-2} + \dots + |A_0| + 1 \right] |A_1| x \\ & + \left[|A_0|^{m-2} + 2 |A_0|^{m-3} + 3 |A_0|^{m-4} + \dots + (m-1) \right] |A_1|^2 x^2 \\ & + \left[|A_0|^{m-3} + \frac{3!}{1! 2!} |A_0|^{m-4} + \frac{4!}{2! 2!} |A_0|^{m-5} + \dots + \frac{(m-1)!}{(m-3)! 2!} \right] |A_1|^3 x^3 \\ & + \left[|A_0|^{m-4} + \frac{4!}{1! 3!} |A_0|^{m-5} + \frac{5!}{2! 3!} |A_0|^{m-6} + \dots + \frac{(m-1)!}{(m-4)! 3!} \right] |A_1|^4 x^4 \\ & + \dots + |A_1|^m x^m \end{aligned} \quad (46)$$

By substituting this result into Eq. (26), one obtains a result of the form

$$(\alpha_0 \cdot \alpha_{n+1})^2 = F_0 + F_1 x + F_2 x^2 + \dots \quad (47)$$

where

$$\begin{aligned}
 F_0 &= \begin{vmatrix} (1-x) & x & 0 \end{vmatrix} |A_0|^n \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix} \\
 &= \begin{vmatrix} (1-x) & x & 0 \end{vmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & (1/2)^n & (1/2)^n \\ 0 & (1/2)^n & (1/2)^n \end{bmatrix} \begin{bmatrix} 1-x \\ x \\ 0 \end{bmatrix} \\
 &= \begin{vmatrix} (1-x) & x & 0 \end{vmatrix} \begin{bmatrix} (1-x) \\ (1/2)^n x \\ (1/2)^n x \end{bmatrix} \quad (48)
 \end{aligned}$$

$$\begin{aligned}
 &= (1-x)^2 + (1/2)^n x^2 \\
 &= 1 - 2x + [1 - (1/2)^n] x^2 = 1 - 2x + x^2 \quad (49)
 \end{aligned}$$

Similarly for large n

$$F_1 = \begin{vmatrix} (1-x) & x & 0 \end{vmatrix} |C_1| |A_1| \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix}$$

where

$$\begin{aligned}
 C_1 &= \{ 1 + |A_0| + |A_0|^2 + |A_0|^3 + \dots \} \\
 &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/4 & 1/4 \\ 0 & 1/4 & 1/4 \end{bmatrix} + \dots \\
 &= \begin{bmatrix} n & 0 & 0 \\ 0 & s_1 & s_1 \\ 0 & s_1 & s_1 \end{bmatrix} \quad (50)
 \end{aligned}$$

$$\text{and} \quad s_1 = 1 + 1/2 + 1/4 + 1/8 + \dots = 2 \quad (51)$$

and

$$\begin{aligned}
 |A_1| & \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix} = \begin{bmatrix} -1 & 1/2 & 1/2 \\ 1 & -1/2 & -1/2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix} \\
 & = \begin{bmatrix} -(1-x) + 1/2 x \\ (1-x) - 1/2 x \\ 0 \end{bmatrix} = \begin{bmatrix} (-1 + 3/2 x) \\ (1 - 3/2 x) \\ 0 \end{bmatrix} \quad (52)
 \end{aligned}$$

so

$$\begin{aligned}
 |C_1||A_1| & \begin{bmatrix} 1-x \\ x \\ 0 \end{bmatrix} = \begin{bmatrix} n & 0 & 0 \\ 0 & 2 & 2 \\ 0 & 2 & 2 \end{bmatrix} \begin{bmatrix} (-1 + 3/2 x) \\ (1 - 3/2 x) \\ 0 \end{bmatrix} \\
 & = \begin{bmatrix} (-1 + 3/2 x) n \\ 2 - 3 x \\ 2 - 3 x \end{bmatrix} \quad (53)
 \end{aligned}$$

and

$$\begin{aligned}
 F_1 & = |(1-x) \ x \ 0| \begin{bmatrix} (-1 + 3/2 x) n \\ 2 - 3 x \\ 0 \end{bmatrix} \\
 & = n (-1 + 3/2 x + x - 3/2 x^2) + 2 x - 3 x^2 \\
 & = -n (1 - 5/2 x + 3/2 x^2) + (2 x - 3 x^2) \quad (54)
 \end{aligned}$$

Similarly

$$F_2 = |(1-x) \ x \ 0| |C_2| |A_1|^2 \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix} \quad (55)$$

where

$$\begin{aligned}
 C_2 & = \{ (n-1) + (n-2) |A_0| + (n-3) |A_0|^2 + \dots \} \\
 & = (n-1) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + (n-2) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix} + (n-3) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/4 & 1/4 \\ 0 & 1/4 & 1/4 \end{bmatrix} + \dots \\
 & = \begin{bmatrix} s_2 & 0 & 0 \\ 0 & s_3 & s_3 \\ 0 & s_3 & s_3 \end{bmatrix} \quad (56)
 \end{aligned}$$

$$\text{and } s_2 = (n-1) + (n-2) + (n-3) + \dots + 1 = n(n-1)/2 \quad (57)$$

$$\text{and } s_3 = (n-1) + (n-2)(1/2) + (n-3)(1/2)^2 + \dots = 2n-4 \quad (58)$$

Evaluation of (55) in the same manner as used for F_1 then gives

$$F_2 = [9/8 x^2 - 15/8 x + 3/4] n^2 + [27/8 x^2 - 9/8 x - 3/4] n + [-9 x^2 + 6 x] \quad (59)$$

Continuing

$$F_3 = \begin{vmatrix} (1-x) & x & 0 \\ |C_3| & |A_1| & 3 \end{vmatrix} \begin{bmatrix} (1-x) \\ x \\ 0 \end{bmatrix} \quad (60)$$

where

$$\begin{aligned} |C_3| &= 1/2 \{ (n-1)(n-2) + (n-2)(n-3) |A_0| + (n-3)(n-4) |A_0|^2 + \dots \} \\ &= 1/2 \begin{bmatrix} s_5 & 0 & 0 \\ 0 & s_6 & s_6 \\ 0 & s_6 & s_6 \end{bmatrix} \end{aligned} \quad (61)$$

and

$$s_5 = 1 \cdot 2 + 2 \cdot 3 + 3 \cdot 4 + \dots + (n-1)(n-2) = n(n-1)(n-2)/3 \quad (62)$$

$$\begin{aligned} s_6 &= (n-1)(n-2) + (n-2)(n-3)(1/2) + (n-3)(n-4)(1/2)^2 + \dots \\ &= 2n^2 - 10n + 16 \end{aligned} \quad (63)$$

This leads to

$$\begin{aligned} F_3 &= 1/2 \{ [-9/8 x^2 + 15/8 x - 3/4] n^3 \\ &\quad + [-27/8 x^2 - 9/8 x + 9/4] n^2 + [63/2 x^2 - 75/4 x - 3/2] n \\ &\quad + [-54 x^2 + 36 x] \} \end{aligned} \quad (64)$$

Upon substituting these results in Eq. (47) one obtains after rearranging and retaining powers of x up to x^3

$$\overline{(a_0 \cdot a_{n+1})^2} = [1 - 2x + 3x^2 + 3x^3] - [1 - 7/4 x - 15/8 x^2] (x n) + [3/4 - 3/2 x] (x n)^2 - [3/8] (x n)^3 + \dots \quad (65)$$

For small x where $x \ll 1$, the higher terms of the polynomial coefficients may be neglected leading to the approximation

$$\overline{(a_0 \cdot a_{n+1})^2} = 1 - x n + 3/4 (x n)^2 - 3/8 (x n)^3 + \dots \quad (66)$$

The orientation function is then obtained using Eq. (15)

$$f(r_{n+1}) = 1 - 3/2 x n + 9/8 (x n)^2 - 9/16 (x n)^3 \quad (67)$$

$$\text{If } \alpha = 3/2 x n \quad (68)$$

this becomes

$$f(r_{n+1}) = 1 - \alpha + \alpha^2/2! - \alpha^3/3! + \dots \quad (69)$$

which is identical with the series expansion for

$$f(r_{n+1}) = e^{-\alpha} \quad (70)$$

Now

$$r_{n+1} = r_n = n d \quad (71)$$

and

$$x = \sin^2 \delta = \delta^2 \quad (72)$$

for small δ . Thus,

$$\alpha = 3/2 x n = 3/2 \delta^2 r_n / d = (3/2 \delta^2 / d) r \quad (73)$$

so

$$f(r) = e^{- (3/2 \delta^2 / d) r} \quad (74)$$

It is apparent that this result is in the form of the Debye-Bueche exponential correlation function

$$f(r) = e^{-r/a} \quad (75)$$

where the correlation distance

$$a = 2d/3 \delta^2 \quad (76)$$

This differs from the two-dimensional correlation distance given by Eq.(10) only in the numerical factors. It is reasonable that the correlation distance should increase with increasing crystal size, d and with decreasing intercrystalline angle δ . For a typical crystal size of 100 \AA and a value of δ^2 of 0.01, one obtains a correlation distance, a , of 6000 \AA which is of the order of magnitude found experimentally. The value of $\delta^2 = .01$ corresponds to $\delta = 0.1$ radians or about 6° which appears reasonable. For this value, $x = \sin^2 \delta \approx \delta^2 = .01$ so that the neglect of terms in x in the polynomial coefficients of Eq. (65) is justified.

It should be pointed out that the exponential correlation function of Eqs.(74 and 75) is a limiting form valid for large n and small δ . The approximations which led to this form (such as the neglect of the coefficients in higher powers of x in Eq. (65)) were not made for necessity, but for simplicity; and it may be desirable to use the more exact result for systems of "coarse" structure where the crystal size, d , is large.

The increase in correlation distance upon annealing and the decrease upon quenching which has been found experimentally may be understood qualitatively, at least, in terms of the corresponding change in the crystal size, d , under these conditions. A quantitative investigation of this relationship should be of interest.

The deviation just given applies only to the case in which the volume elements are separated from each other along the direction of the lattice row. However, the lattice is an artifact of the calculation and not a property of the material. Consequently the lattice direction is completely arbitrary, and the result should be valid for volume elements having a line of separation in any direction.

APPENDIX I

Consider the special case

$$\overline{(a_0 \cdot a_3)^2} = \overline{\left[\sum_i \sum_j [a_{1i}]_3 [a_{ij}]_2 [a_{j1}]_1 \right]^2} \quad (\text{AI-1})$$

Now let

$$\beta_{i1} = \sum_j [a_{ij}]_2 [a_{j1}]_1$$

or

$$\begin{aligned} |B| &= |T_2| \begin{bmatrix} a_{11} \\ a_{21} \\ a_{31} \end{bmatrix} \\ &= \begin{bmatrix} \cos \delta & -\sin \delta \cos \phi_2 & \sin \delta \sin \phi_2 \\ \sin \delta & \cos \delta \cos \phi_2 & -\cos \delta \sin \phi_2 \\ 0 & \sin \phi_2 & \cos \phi_2 \end{bmatrix} \begin{bmatrix} \cos \delta \\ \sin \delta \\ 0 \end{bmatrix} \\ &= \begin{bmatrix} \cos^2 \delta - \sin^2 \delta \cos^2 \phi_2 \\ \sin \delta \cos \delta + \sin \delta \cos \delta \cos \phi_2 \\ \sin \delta \sin \phi_2 \end{bmatrix} \end{aligned} \quad (\text{AI-2})$$

Similarly

$$\gamma_{11} = \sum_i [a_{1i}]_3 [\beta_{i1}]$$

or

$$\begin{aligned} C &= |a_{11} \ a_{12} \ a_{13}| \ 3 \begin{bmatrix} \beta_{11} \\ \beta_{21} \\ \beta_{31} \end{bmatrix} \\ &= |\cos \delta - \sin \delta \cos \phi_3 \ \sin \delta \sin \phi_3| \begin{bmatrix} \cos^2 \delta - \sin^2 \delta \cos \phi_2 \\ \sin \delta \cos \delta + \sin \delta \cos \delta \cos \phi_2 \\ \sin \delta \sin \phi_2 \end{bmatrix} \\ &= \cos^3 \delta - \sin^2 \delta \cos \delta \cos \phi_2 - \sin^2 \delta \cos \delta \cos \phi_3 - \sin^2 \delta \cos \delta \cos \phi_2 \cos \phi_3 \\ &\quad + \sin^2 \delta \sin \phi_2 \sin \phi_3 \end{aligned} \quad (\text{AI-3})$$

Then $\overline{(a_0 \cdot a_3)^2} = C^2$

$$\begin{aligned}
&= \overline{\cos^6 \delta} + \overline{\sin^4 \delta \cos^2 \delta \cos^2 \phi_2} + \overline{\sin^4 \delta \cos^2 \delta \cos^2 \phi_3} \\
&+ \overline{\sin^4 \delta \cos^2 \delta \cos^2 \phi_2 \cos^2 \phi_3} + \overline{\sin^4 \delta \sin^2 \phi_2 \sin^2 \phi_3} \\
&- 2 \overline{\sin^2 \delta \cos^4 \delta \cos \phi_2} - 2 \overline{\sin^2 \delta \cos^4 \delta \cos \phi_3} \\
&- 2 \overline{\sin^2 \delta \cos^4 \delta \cos \phi_2 \cos \phi_3} + 2 \overline{\sin^2 \delta \cos^3 \delta \sin \phi_2 \sin \phi_3} \\
&+ 2 \overline{\sin^4 \delta \cos^2 \delta \cos \phi_2 \cos \phi_3} + 2 \overline{\sin^4 \delta \cos^2 \delta \cos^2 \phi_2 \cos \phi_3} \\
&+ 2 \overline{\sin^4 \delta \cos \delta \sin \phi_2 \cos \phi_2 \sin \phi_3} + 2 \overline{\sin^4 \delta \cos^2 \delta \cos \phi_2 \cos^2 \phi_3} \\
&- 2 \overline{\sin^4 \delta \cos \delta \sin \phi_2 \cos \phi_2 \cos \phi_3} - \overline{\sin^4 \delta \cos \delta \sin \phi_2 \cos \phi_2 \sin \phi_3 \cos \phi_3}
\end{aligned} \tag{AI-4}$$

Since the ϕ_i 's vary randomly and are not correlated with each other

$$\overline{\sin^2 \phi_i} = \overline{\cos^2 \phi_i} = 1/2 \tag{AI-5}$$

and

$$\overline{\sin^2 \phi_i \sin^2 \phi_j} = \overline{\sin^2 \phi_i} \overline{\sin^2 \phi_j} = \overline{\cos^2 \phi_i} \overline{\cos^2 \phi_j} = \overline{\cos^2 \phi_i} \overline{\cos^2 \phi_j} = 1/2 \cdot 1/2 = 1/4 \tag{AI-6}$$

$$\overline{\sin \phi_i} = \overline{\cos \phi_i} = \overline{\sin \phi_i \cos \phi_i} = \overline{\sin^2 \phi_i} \overline{\cos \phi_i} = \overline{\sin \phi_i \cos^2 \phi_i} = \overline{\sin^3 \phi_i} \overline{\cos \phi_i} \tag{AI-7}$$

$$= \overline{\sin \phi_i \cos^3 \phi_i} = 0$$

Thus, the cross-product terms are all zero and

$$\overline{(a_0 \cdot a_3)^2} = \overline{\cos^6 \delta} + 5/4 \overline{\sin^4 \delta \cos^2 \delta} + 1/4 \overline{\sin^4 \delta} \tag{AI-8}$$

Since the cross-products vanish, the same result may be obtained by squaring the matrix elements and averaging them before multiplying. That is:

$$\overline{(a_0 \cdot a_3)^2} = \sum_i \sum_j [\overline{a_{1i}^2}]_3 [\overline{a_{ij}^2}]_2 [\overline{a_{j1}^2}]_1 \tag{AI-9}$$

where, for example,

$$\begin{aligned}
\left| \overline{a_{ij}^2} \right| &= \begin{bmatrix} \overline{\cos^2 \delta} & \overline{\sin^2 \delta \cos^2 \phi_2} & \overline{\sin^2 \delta \sin^2 \phi_2} \\ \overline{\sin^2 \delta} & \overline{\cos^2 \delta \cos^2 \phi_2} & \overline{\cos^2 \delta \sin^2 \phi_2} \\ 0 & \overline{\sin^2 \phi_2} & \overline{\cos^2 \phi_2} \end{bmatrix} \\
&= \begin{bmatrix} \overline{\cos^2 \delta} & 1/2 \overline{\sin^2 \delta} & 1/2 \overline{\sin^2 \delta} \\ \overline{\sin^2 \delta} & 1/2 \overline{\cos^2 \delta} & 1/2 \overline{\cos^2 \delta} \\ 0 & 1/2 & 1/2 \end{bmatrix}
\end{aligned} \tag{AI-10}$$

So

$$\begin{aligned}
 \overline{(u_2 \cdot u_3)^2} &= \begin{vmatrix} \cos^2 \delta & 1/2 \sin^2 \delta & 1/2 \sin^2 \delta \\ \sin^2 \delta & 1/2 \cos^2 \delta & 1/2 \cos^2 \delta \\ 0 & 1/2 & 1/2 \end{vmatrix} \\
 &= \cos^2 \delta \begin{vmatrix} \cos^4 \delta + 1/2 \sin^4 \delta \\ 3/2 \sin^2 \delta \cos^2 \delta \\ 1/2 \sin^2 \delta \end{vmatrix} \\
 &= \cos^6 \delta + 1/2 \sin^4 \delta \cos^2 \delta + 3/4 \sin^2 \delta \cos^2 \delta + 1/4 \sin^4 \delta \\
 &= \cos^6 \delta + 5/4 \sin^4 \delta \cos^2 \delta + 1/4 \sin^4 \delta
 \end{aligned} \tag{AI-11}$$

This is identical with Eq.(AI-8) verifying the identity of Eqs.(AI-1) and (AI-9). These are a special case of Eqs. (22) and (23) which may be proved by an extension of the above procedure.

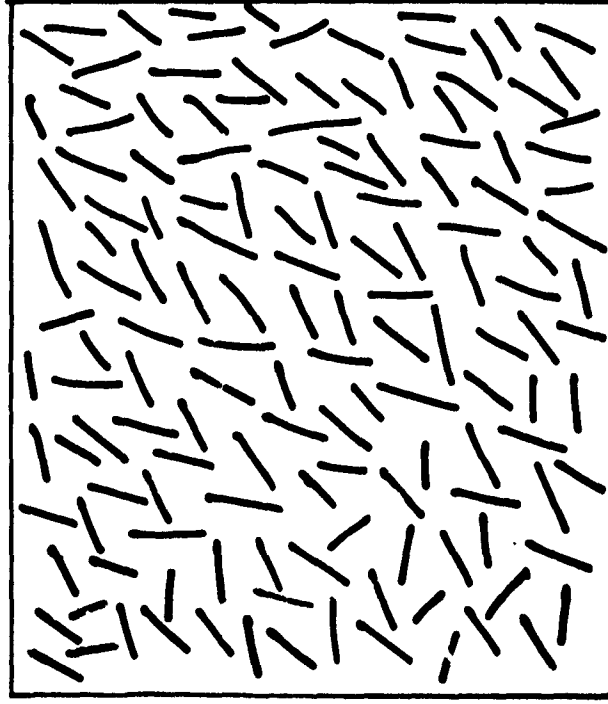
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CAPTIONS FOR FIGURES

1. Random and correlated orientation fluctuation.
2. The variation of the orientation correlation function $f(r)$ with r .
3. Random walk correlation in one-dimension
4. The lattice model for correlated orientation.
5. Random walk correlation with angular fluctuations in three dimensions.

RANDOM



CORRELATED

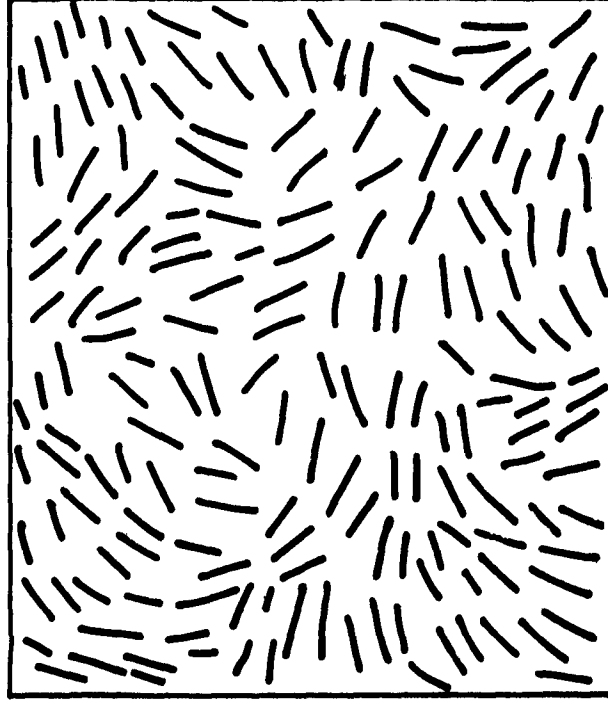


FIG. 1

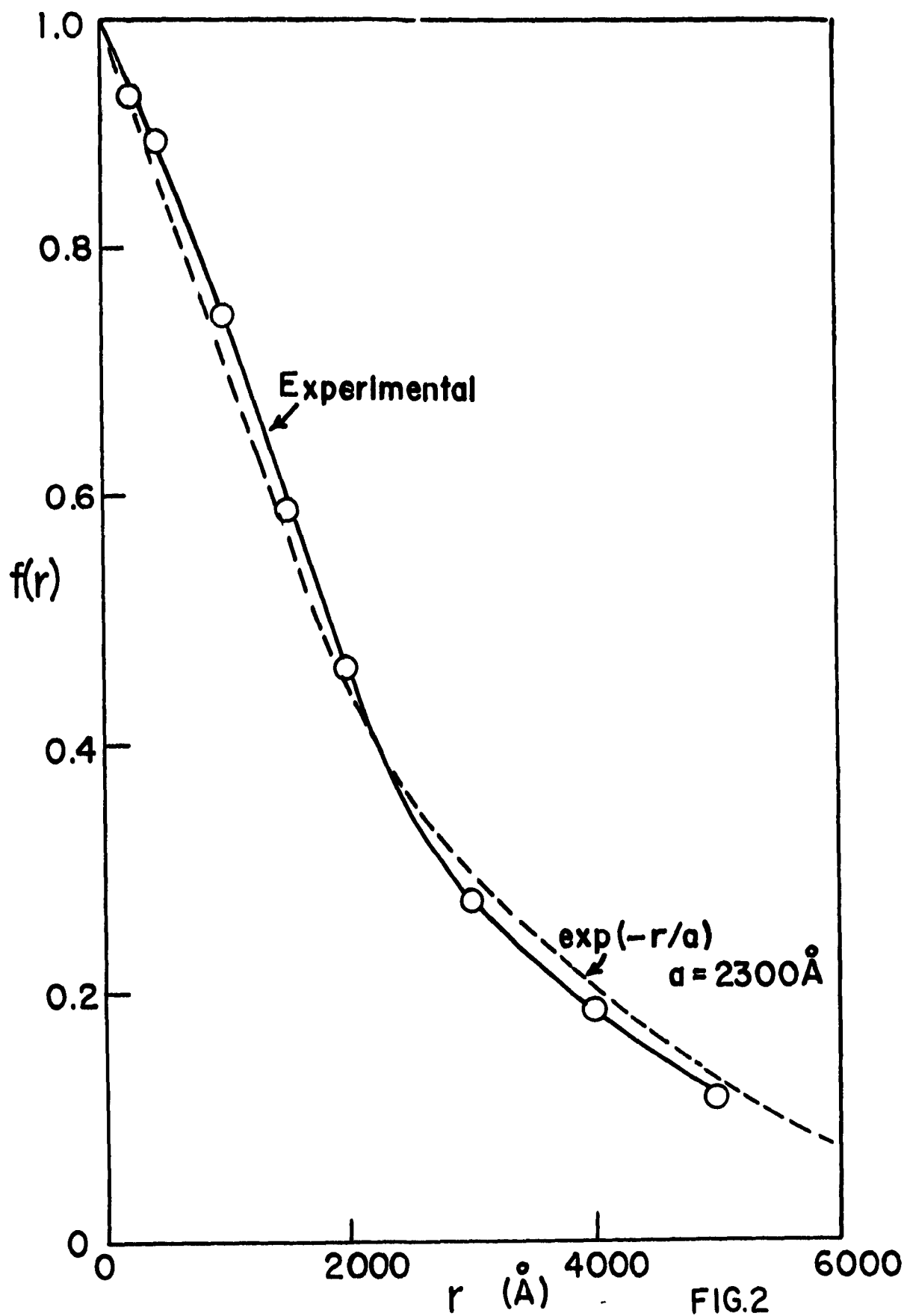
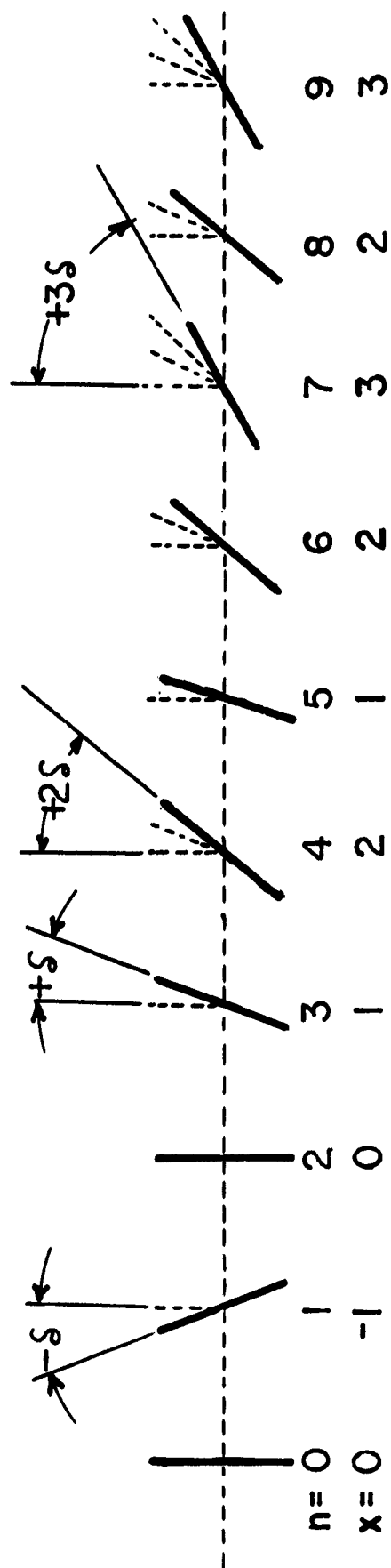


FIG.2



$$\theta = x s$$

FIG. 3

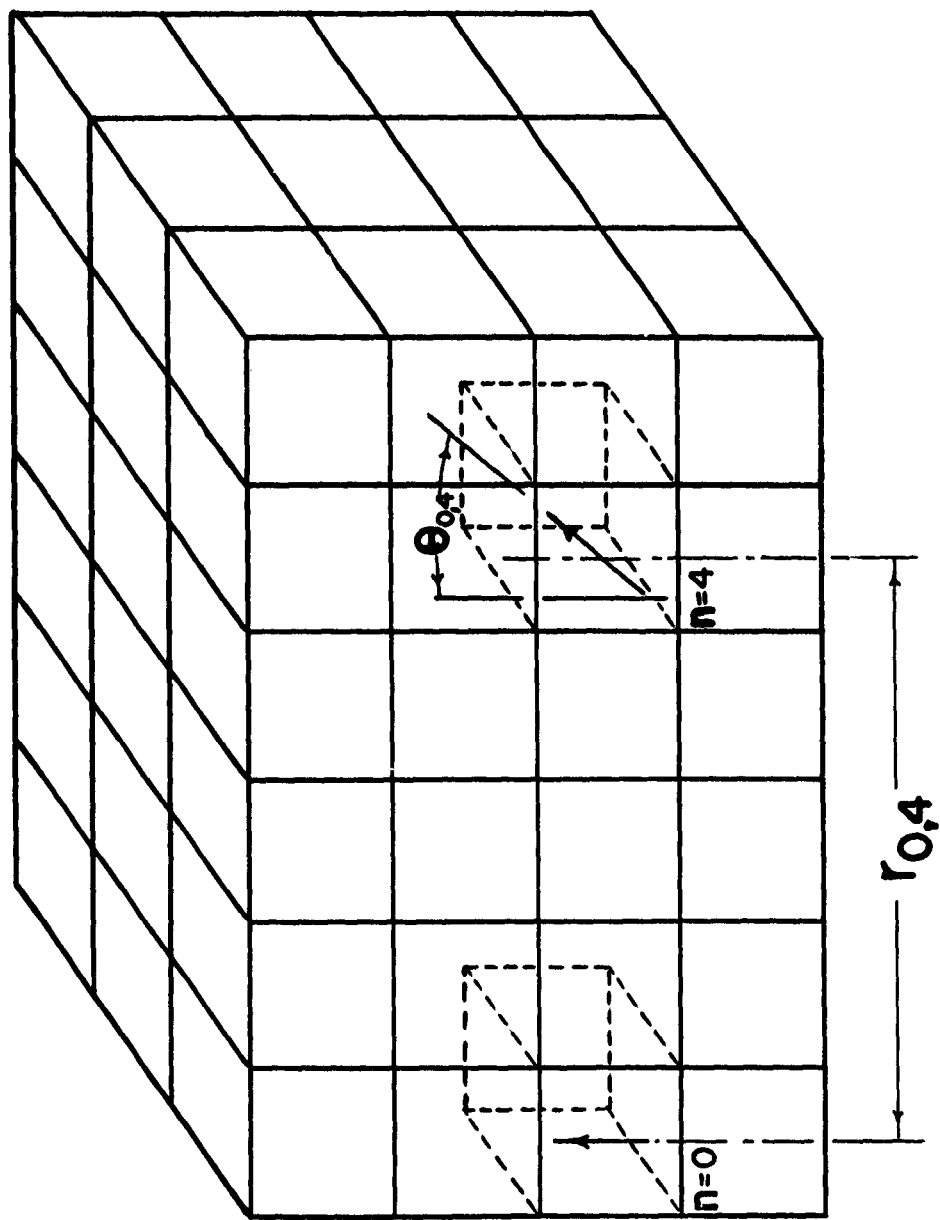


Fig. 4

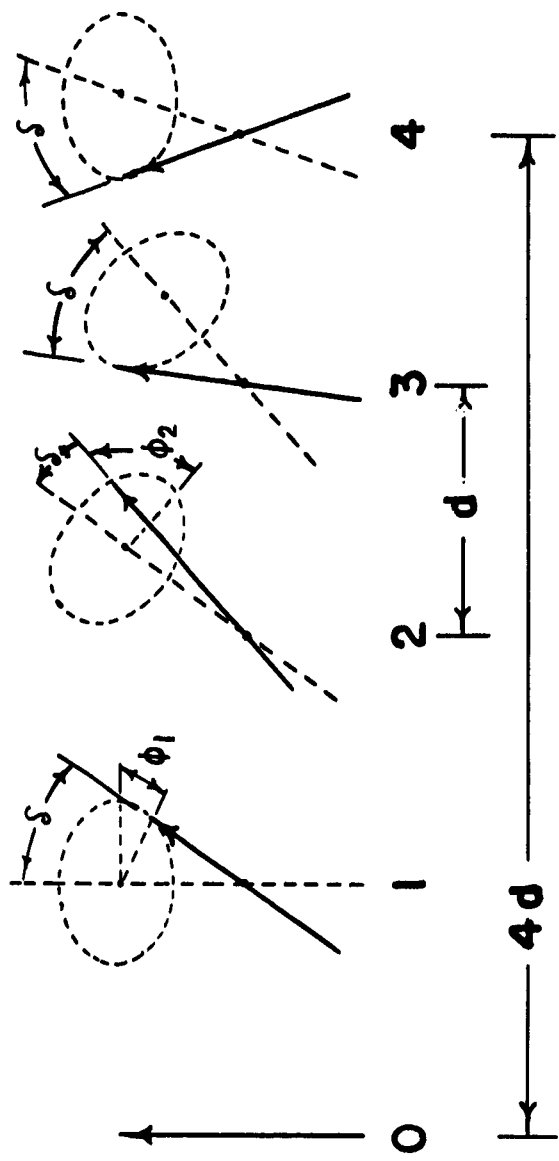


Fig. 5